# Electrochemically Active Polymers for Electrochemical Energy Storage: Opportunities and Challenges

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ABSTRACT: Polymers have a particularly important place in electrochemical energy storage (EES), not just as the electrolyte, as has been a large focus for solid-state batteries, but also as the electrode. This Viewpoint will introduce how electrochemically active polymers (EAPs) are utilized in electrochemical energy storage with an emphasis on battery cathodes. Recent advances in high capacity EAPs and selected challenges (high voltage stability and ion transport) are presented. Should these needs be met, the resulting electrode would bear a high capacity, energy, power, and cycle life. The low cost, potential application in flexible EES, and synthetic versatility of EAPs offer many unique aspects relative to conventional metal oxides. In composites with metal oxides, EAPs can be used as a means to boost ionic and electronic conductivity. Promising examples regarding high capacity polymeric sulfur electrodes, electrochemically stable polyaniline/polyacid complexes, porous polyaniline/V_2O_5 electrodes, and hydrogel-based electrodes are highlighted.
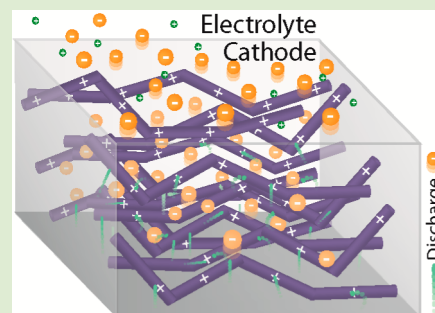
Electrochemical energy storage (EES) has become increasingly important, as new technologies are needed to power electric vehicles and load-level energy derived from intermittent sources such as wind or solar.[1,2] Polymers have a particularly important place in EES not just as the electrolyte, as has been a large focus for solid-state batteries, but also as the electrode. There are many motivations for utilizing electrochemically active polymers (EAPs) as electrodes. They can be derived from domestic feedstock and do not rely on the procurement of critical materials. Cobalt, for example, is used in $LiCoO_2$ battery cathodes and is not produced domestically in the U.S.[3] Polymers enable electrodes for flexible energy storage,[4] can be functionalized synthetically with ease,[5−7] and, if conjugated, lend conductivity to otherwise insulating composites.[8−10]

Accordingly, this Viewpoint will introduce how EAPs are utilized as electrodes in EES, with an emphasis on application in batteries. Several thorough reviews exist that cover electrodes for EES that focus on typical classes of EAPs (polyanilines, polypyrroles, polythiophenes, organic radicals, etc.).[4,11−15] Here, this Viewpoint will begin with recent advances in high capacity EAP electrodes and will then finish with a selection of current challenges in EAP electrodes (stability at high voltages and ion transport).

EES using EAPs was demonstrated in the late 1980s as polyaniline-lithium batteries and as polythiophene-based capacitors.[16−18] Since then, this concept has been extended to broad classes of other conjugated polymers for use as cathodes and anodes in EES. p-type conjugated polymers are suitable candidates for cathodes or positive electrodes, whereas n-type conjugated polymers are used as anodes or negative electrodes. There are many challenges for n-type EAPs, particularly regarding their electrochemical stability and high impedance.[11,19] On the other hand, much of the ongoing work in EAPs for EES has focused on p-type conjugated polymers, perhaps because they exhibit relatively more stability.

Energy storage, using a p-type EAP is achieved via the exchange of dopant anions and electrons during charge and discharge. A p-type polymer is generally neutral in the discharged state and positively charged in the doped state.[11,20] The general redox chemistry of a nonaqueous p-type polymer−Li cell in discharge is shown below

Cathode:

$$[\text{Poly}^{n+}][A^-]_n + ne^- \rightarrow \text{Poly} + nA^-$$
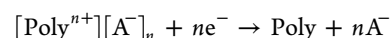
Anode:

$$n\text{Li} \rightarrow n\text{Li}^+ + ne^-$$
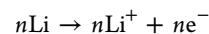
As the cathode is discharged, oxidized p-type polymer doped with anions ($[\text{Poly}^{n+}][A^-]_n$) takes up electrons and releases dopant anions into the electrolyte. At the anode, lithium (or carbon) releases lithium ions into the electrolyte and gives up electrons. Upon charging, the processes are reversed. Electrolyte is required to facilitate the migration of lithium ions and dopant anions across the cell. Other mechanisms of charge storage are possible for redox-active pendant groups, discussed later.

EAPs have been widely studied as electrode materials for batteries and electrochemical capacitors, both of which are widely different in terms of energy and power.[21] Batteries have high energy and low power, and electrostatic capacitors have low energy and high power. Electrochemical capacitors (ECs)
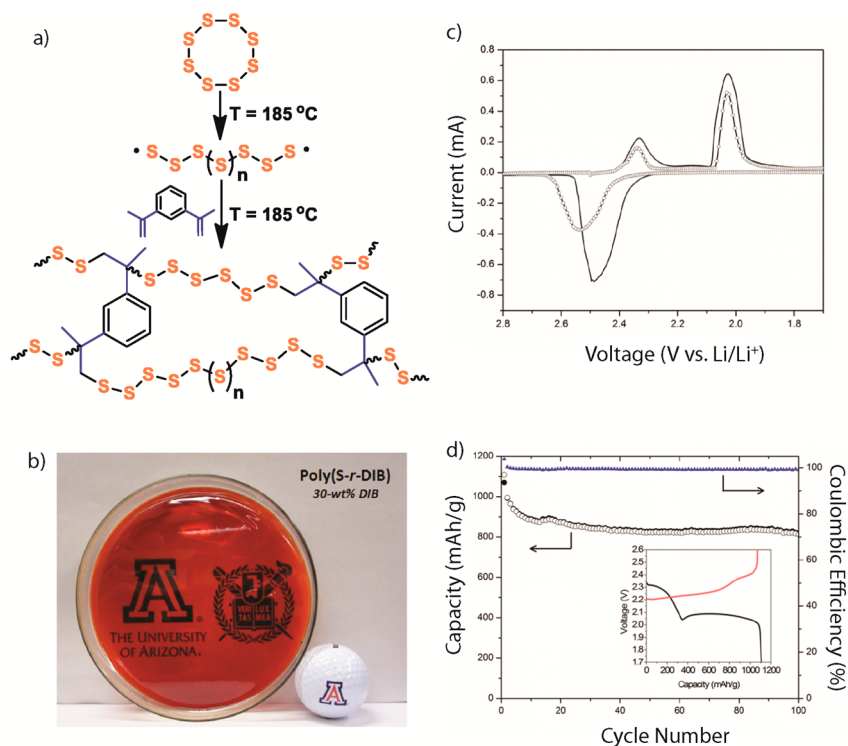
Figure 1. (a) Synthetic scheme for the inverse vulcanization of elemental sulfur and 1,3-diisopropenylbenzene (DIB). (b) Transparent glass film of poly(S-r-DIB) with 30 wt % DIB thermally cured on a 25 g scale. (c) Cyclic voltammetry of pure sulfur (solid black line) and poly(S-r-DIB) (10 wt % DIB, open circles) at a scan rate of 20 μV/s. (d) Battery cycling data for poly(S-r-DIB) (10 wt % DIB, C/10 rate) showing the discharge capacity (open circles), charge capacity (filled circles), and Coulombic efficiency (blue triangles) with the inset showing a typical charge/discharge profile. (Reprinted with permission from MacMillan Publishers Ltd.: *Nature Chemistry*, ref 30, copyright 2013.)

are viewed as a bridge to the power and energy gap between batteries and electrostatic capacitors.[11] The time scale of discharge is also vastly different.[22] Using electric vehicles as an example, batteries provide energy for the drive train over a time scale of hours, and ECs harvest and store energy from regenerative braking (tens of seconds). A battery has a typical discharge time of 0.3−3 h, specific energy of up to 230 Wh/kg, specific power up to 1500 W/kg, and cycle life of 500−2000.[21,23] LiCoO₂ and LiFePO₄ are examples of Li-ion battery cathodes on the commercial market.[24] On the other hand, an EC has a typical discharge time of 0.3−30 s, specific energy of 1−10 Wh/kg, specific power of ∼1000 W/kg, and cycle life of 100 000.[21] However, for conjugated polymers the cycle life can be on the order of ∼1000 because of issues with electrochemical stability and volumetric expansion/contraction.[11,20]

Typical reported capacities of p-type EAPs, such as polyanilines and polypyrroles, fall in the range of 80−150 mAh/g,[13,14] as compared to theoretical capacities for LiCoO₂ and LiFePO₄ of 137 and 170 mAh/g, respectively.[23] Therefore, quite a bit of attention has been devoted to the exploration of EAPs bearing a high theoretical capacity. The general focus has been to maximize the amount of charge exchanged per mass.

One approach to increasing theoretical capacity in EAPs is to use a redox-active side chain or pendant group.[7,25,26] For example, Conte et al. synthesized an electrochemically polymerizable thiophene derivative with a redox-active N,N,N′,N′-tetraalkylated-p-phenylenediamine (TAPD) side chain; redox activity of both the side chain and polymer backbone was demonstrated.[27] This derivative can potentially store up to 229 mAh/g (or 2.6 electrons per repeat unit), although the actual performance in a battery was not reported.

Oyaizu et al. recently reported a 2,2,5,5-tetramethyl-3-oxiranyl-3-pyrrolin-1-oxyl-functionalized poly(ethylene oxide) with a theoretical capacity of 147 mAh/g.[28] The material exhibited an operating voltage of 3.7 V vs Li/Li⁺ and retained >80% of its initial capacity after 1000 cycles. Nokami et al. reported the performance of pyrene-4,5,9,10-tetraone bound to an acrylate copolymer, capable of storing four electrons and four lithium cations per repeat unit.[29] A capacity of 193 mAh/g was retained after 500 cycles.[29]

One high capacity EAP for EES to emerge recently is not conjugated at all but rather is a cross-linked polymeric sulfur,[30] which takes advantage of Li−S battery chemistry. Sulfur can store up to two electrons per sulfur atom, which gives it a relatively high theoretical capacity (1673 mAh/g) via the following redox chemistry[31]

$$S_8 + 16Li^+ + 16e^- \rightarrow 8Li_2S$$
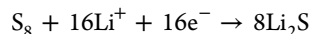
However, sulfur's theoretical capacity is rarely achieved in practice because of the formation and dissolution of lithium sulfide species (Li_2S_n) into the electrolyte, as well as volumetric expansion and contraction.[32−34] Accordingly, cross-linked polymeric sulfur should prevent the release of these lithium sulfides and exhibit enhanced cycle life.

The cross-linked polymeric sulfur was synthesized using inverse vulcanization, where molten polymeric sulfur was cross-linked with a divinylic monomer (diisopropenylbenzene, DIB) to form poly(S-r-DIB) (Figure 1).[30] Without this cross-linker, polymeric sulfur depolymerizes at room temperature. Cross-linked polymeric sulfur exhibited very similar electrochemical behavior to S₈, and the cross-linked polymeric sulfur electrode exhibited a high capacity of 823 mAh/g after 100 cycles, which
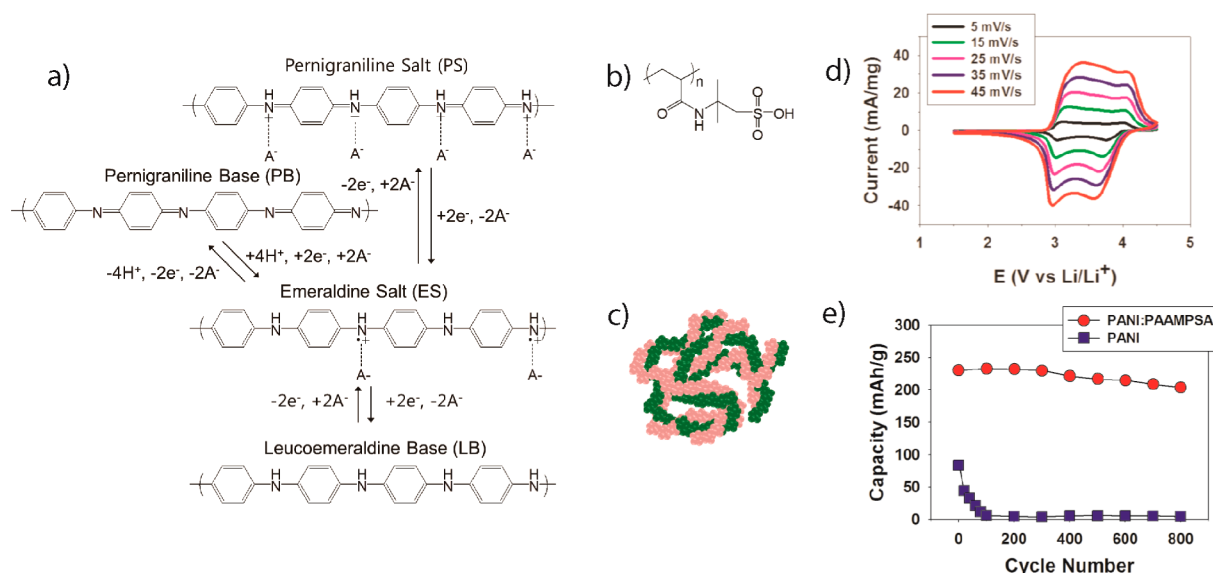
Figure 2. (a) Various polyaniline (PANI) oxidation states. (b) Poly(2-acrylamido-2-methyl-1-propanesulfonic acid), PAAMPSA. (c) An idealized cartoon of the PANI:PAAMPSA complex. (d) Cyclic voltammetry of a PANI:PAAMPSA positive electrode in 0.5 M LiClO$_4$ in propylene carbonate. (e) Discharge capacity of PANI:PAAMPSA and PANI homopolymer electrodes over 800 cycles between 1.5 and 4.5 V vs Li/Li$^+$. (Reproduced from ref 41 with permission from the PCCP Owner Societies.)

is greater than that of S$_8$ (≈200 mAh/g after 40 cycles).[35] Lacking a conjugated structure, polymeric sulfur is not conductive so carbon black was added to the electrode. Future explorations of this material would greatly benefit from efforts to control conductivity to minimize the additive content.

In recent work, EAPs have been applied as conductive additives to elemental sulfur electrodes. Fu and Manthiram demonstrated a polypyrrole:poly(2-acrylamido-2-methyl-1-propanesulfonic acid) complex that was used as an additive in sulfur cathodes for Li−S batteries.[34] Sulfur was synthesized in the presence of the complex to achieve an electrode of 75 wt % sulfur and 25 wt % complex. The electrode retained a capacity of 500 mAh/g after 50 cycles, which was attributed to the complex's mixed ionic and electronic conductivity.

The prior discussion presented several recent EAPs bearing a high theoretical capacity. However, an electrode's practical capacity is often limited by electrochemical stability and ion transport, among other considerations. Next, we will focus upon electrochemical stability at high voltages, which has implications on the practical capacity that can be achieved, especially in p-type conjugated polymers. One route to boosting capacity (and, in turn, energy) in p-type conjugated polymers is to target higher doping levels, which often requires the application of high voltages in nonaqueous electrolyte.[1,36] Ideally, a conjugated polymer could store one (or more, in some cases) charge per repeat unit, but typical reversible doping levels for polyanilines, polypyrroles, and polythiophenes are 0.3−0.5.[11] At higher doping levels, EAPs often lose reversibility via unwanted side reactions. Another motivation for identifying and utilizing EAPs that are stable or reversible under high potentials is that they could possibly be used in composites with high-voltage cathode materials such as LiMn$_{1.5}$Ni$_{0.5}$O$_4$, LiCoPO$_4$, and LiNiPO$_4$, which have operating voltages of 4.7, 4.8, and 5.2 V vs Li/Li$^+$, respectively.[36]

Polyaniline is one widely explored example of electrochemical instability at high voltages; several oxidation states exist depending on applied potential and whether the process is occurring in an aqueous or nonaqueous environment[37−39]

(Figure 2a). Polyaniline reversibly switches between fully reduced leucoemeraldine base and half-doped emeraldine salt in both environments, transferring electrons and dopant anions in the process with a theoretical capacity of 147 mAh/g. Under nonaqueous conditions, oxidation beyond half-doped emeraldine salt results in the irreversible formation of pernigraniline base, and polyaniline's capacity rapidly fades upon cycling because protons are not available in the aprotic electrolyte for the reverse reaction to proceed.[40] Because of this irreversibility, nonaqueous polyaniline electrodes have been generally limited to potentials less than 3.5 V vs Li/Li$^+$. Commercially, polyaniline's pernigraniline base/emeraldine salt redox chemistry has been harnessed in a polyaniline-lithium battery that was once available from Bridgestone-Seiko in the 1980s.[18]

In recent work, we have reported a polyaniline:polyacid complex that was electrochemically stable up to 4.5 V vs Li/Li$^+$ and reversibly accessed both fully reduced and fully oxidized states of polyaniline (leucoemeraldine base and pernigraniline salt, theoretical capacity of 294 mAh/g) (Figure 2b−d).[41] Aniline monomer was polymerized in the presence of a strong polyacid, in this case, poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAAMPSA). The reversible capacity of the polyaniline/PAAMPSA electrode was as high as 230 mAh/g$_{polyaniline}$. When cycled under identical conditions (1.5−4.5 V vs Li/Li$^+$), polyaniline:PAAMPSA retained 88.5% of its initial capacity, whereas polyaniline homopolymer retained only 5.5%. The highest specific energy obtained for polyaniline/PAAMPSA was 700 mWh/g, which was achieved at a discharge current of 1 C. The highest specific power exhibited by the material was 33600 mW/g$_{polyaniline}$ and was achieved at a discharge current of 50 C. (Here, a discharge current of 1 C was the current required to discharge the theoretical capacity of the electrode in one hour.) The key to polyaniline/PAAMPSA's electrochemical stability lay in the noncovalent interactions between the two polymers, where PAAMPSA itself acted as the dopant. The interactions were so favorable that the pernigraniline salt form of polyaniline was observed, where polyaniline was fully charged and doped. This is in significant contrast to

polyaniline homopolymer, where the dopant is often a small anion, and pernigraniline salt has been observed only in very controlled conditions (ionic liquids, <pH 1).[42,43] This level of electrochemical stability has not been achieved with other methods of blending polyaniline with polyanion,[41,44,45] so it can be inferred that synthesis of polyaniline in the presence of a polyanion produces a complex of unique morphology and structure.

Polyaniline/PAAMPSA, though electrochemically stable, does suffer from the presence of nonelectroactive PAAMPSA, which comprises 75% of the electrode's mass. Clearly, it will be important to reduce the content of PAAMPSA, which might require different polymerization conditions or a different polyanion altogether. Even so, low capacities in EAPs can be acceptable if they are stable up to high voltages and particularly if they are used to enhance conductivity as composites with highly electroactive metal oxides. For instance, it has been recently demonstrated that poly(3-hexylthiophene)-b-poly-(ethylene oxide) successfully conducted ions and electrons, boosting the performance of a $LiFePO_4$ cathode.[10,46]

Other approaches to enhancing stability at high voltages in conjugated polymers have focused on conjugated polymers having electron-rich fused ring backbones. Examples include poly(dithieno[3,2-b:2',3'-d]pyrroles),[47] poly(3,4-ethylenedithiothiophene),[48] and poly(benzo[1,2-b;4,5-b']dithiophene);[49] while not widely explored for EES as of yet, these classes of conjugated polymers are potentially promising.

Besides electrochemical stability, ion transport is particularly important because it influences the fraction of electrode material that is electrochemically accessible and subsequently the capacity, energy, and power. The ion transport of dopant ions becomes critical, especially in thicker (>100 μm) electrodes.[22] Porosity or nanostructuring is one approach to enhancing ion transport and has been explored widely in high surface area carbon substrates,[50−52] porous cellulosic substrates,[53−55] and 1D nanostructures.[56−59] While porosity can increase the electrode's specific power and energy (which have a basis of mass), the power and energy density (which have a basis of volume) can decrease owing to inactive void space; therefore, it is important to engineer an electrode's porosity to suit a particular application's needs (low volume vs low mass).

In our own work, we have shown that porous polyaniline/V_2O_5 layer-by-layer (LbL) composite electrodes have higher specific energy and power than dense, nonporous analogs (Figure 3).[40,60] Notably, no significant losses in energy density and power density were observed. V_2O_5 is a battery cathode material that has a high theoretical capacity but low electronic and ionic conductivity. Polyaniline, on the other hand, exhibits both electronic and ionic conductivity. It was shown that the polyaniline/V_2O_5 LbL composite electrodes, where polyaniline was synthesized via oxidative polymerization, were dense and somewhat susceptible to ion transport limitations, characterized by a decline in capacity vs thickness. By replacing polyaniline with polyaniline nanofibers, the capacity (320 mAh/g), specific energy (886 mWh/g), and specific power (4000 mW/g) of the resulting porous electrode increased by factors of 3, 40, and 4, respectively. This was attributed to the formation of a porous architecture (void fraction = 0.85) brought about by the random adsorption of polyaniline nanofibers. After 100 cycles, the electrode maintained 75% of its initial capacity, and the main source of degradation was attributed to the irreversible formation of pernigraniline base, despite limiting the upper voltage to 3.5 V vs Li/Li+.
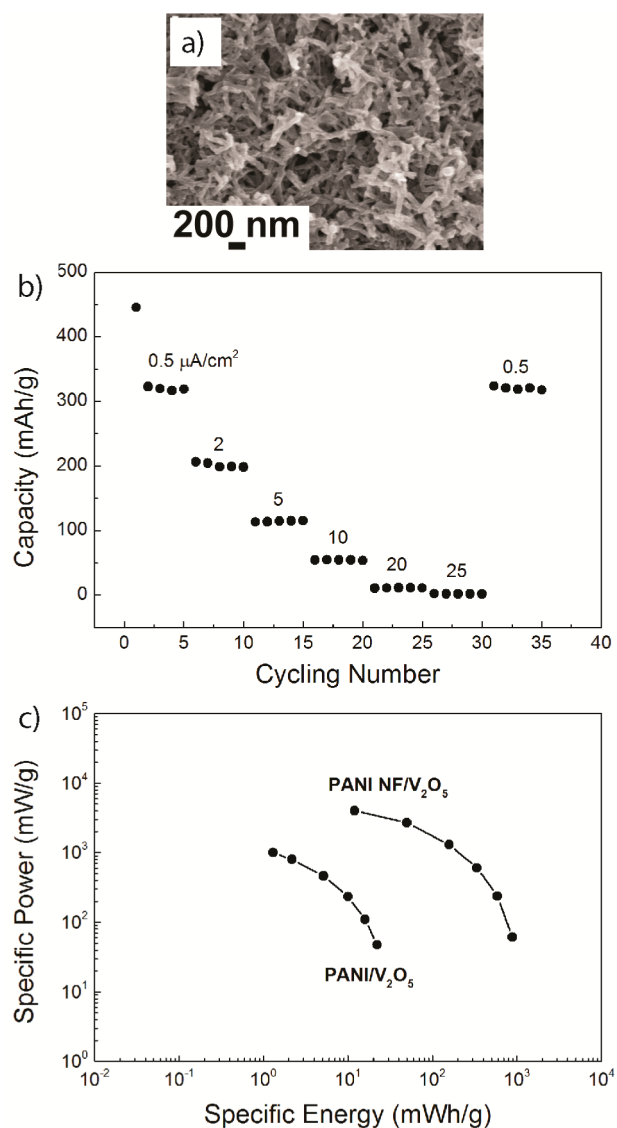

Figure 3. (a). Scanning electron microscopy image of the surface of a polyaniline nanofiber (PANI NF)/V_2O_5 layer-by-layer (LbL) cathode and (b) its capacity. (c) Ragone plot for a porous (PANI NF/V_2O_5) and analogous nonporous (PANI/V_2O_5) LbL cathodes. Lithium ribbon was the anode, and the electrolyte was 0.5 M $LiClO_4$ in propylene carbonate. (Reproduced from ref 60 with permission from The Royal Society of Chemistry.).

Polyaniline nanofibers have also been used as composites with multiwall carbon nanotubes (MWNTs) to form porous electrodes for use as battery cathodes.[61] MWNTs were added to the system to improve the electrical conductivity from 0.8 S/cm (polyaniline nanofibers alone) to 4.1 S/cm (MWNT/polyaniline nanofiber composite). The resulting cathodes retained a volumetric capacity of 210 mAh/cm^3 after 1000 cycles.

Another approach to controlling ion transport is to use a gel-like morphology, where ions transport much as they would in a liquid rather than a solid.[62−64] One recent example from Pan et al. shows the viability of such an approach in the application of electrochemical capacitors (Figure 4).[65] Aniline monomer was polymerized in the presence of phytic acid to produce a high surface area, porous hydrogel. The specific capacitance was 480 F/g, of which 83% was retained after 10 000 cycles. Unlike
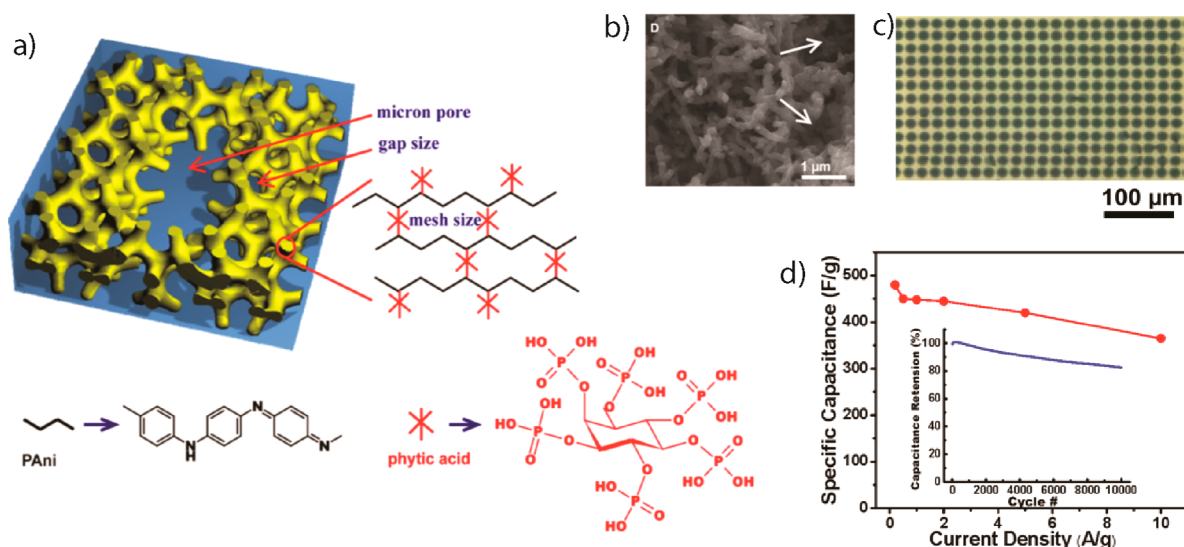
Figure 4. (a) Polyaniline/phytic acid hydrogel electrode. (b) SEM image showing interconnected polyaniline nanofibers. (c) Optical micrograph of inkjet printed hydrogel dots. (d) Cycling tests for the hydrogel electrodes in 1 M H$_2$SO$_4$. The water content of the electrode was 92.6%. (Reproduced from ref 65 with permission. Copyright 2012 National Academy of Sciences, USA.)

prior hydrogel-based electrodes, these were conductive (0.11 S/cm) and micropatternable.

EAPs are potentially vital to the development of the next generation of EES technologies. Their low cost, potential application in flexible EES, and synthetic versatility offer many unique aspects relative to conventional metal oxides. Ideally, next-generation EAPs should possess a high doping level, electrochemical stability, processability, and good ion transport. Should these needs be met, the resulting EAP would bear a high capacity, energy, power, and cycle life. In composites with metal oxides, EAPs can be used as a means to boost ionic and electronic conductivity. Promising examples regarding high capacity polymeric sulfur electrodes, electrochemically stable polyaniline/polyacid complexes, porous polyaniline/V$_2$O$_5$ electrodes, and hydrogel-based electrodes were highlighted. The future for polymer-based electrodes for EES is particularly exciting, given the wealth of ongoing parallel work in solid polymer electrolytes. Conceivably, the confluence of both fields could result in a low cost, high performance, all-polymer battery or capacitor for applications such as flexible energy storage.

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Author Contributions
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Notes
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